Geochemical Cycling and the Oceans  
EAS 302  
Lecture 33

Geochemical Cycling

Paraphrasing Stanley: many of the environmental changes affecting the Earth are ultimately caused by chemical changes.
- e.g.:
  - surface temperature is controlled in part by the concentration of atmospheric CO₂.
  - Transition from a reducing to an oxidizing atmosphere. This made higher life possible. The Earth is not a static place.
- Changes such as these reflect changes in the manner and rates at which elements cycle between reservoirs. As it turns out, cycling of oxygen and carbon are closely linked. Let's examine this chemical cycling in more detail.

Some Definitions
Reservoir

• *Mass of material that is potentially subject to a common set of chemical interactions.*
  – Reservoirs may have distinct, sharp boundaries:
    • Example: *the oceans, the atmosphere*
  – Alternatively, a reservoir may be dispersed throughout some region of the Earth.
    • Example: "sedimentary organic carbon"
      – sediments are dispersed throughout the crust, and organic carbon is dispersed through those sediments. However, all sedimentary organic carbon is formed through burial of the remains of organisms, and is subject to oxidation and conversion to CO$_2$ upon erosion.
    • Sometimes speak of a reservoir of a single element, or a single form of an element.

Flux

• A flux represents a flow of material from one reservoir to another.
  – This may reflect physical movement of the material.
    • e.g.: subduction zone volcanism is a mantle-to-crust flux.
  – Alternatively, it may represent only a chemical change.
    • Organic carbon may be oxidized to carbonate and remain in the same place. Hence a flux may simply be a chemical reaction.
    • A flux may involve both physical movement and chemical reaction.
  • The flux into a reservoir (or the reservoir from which the flux comes) is called a *source*; the flux out is called a *sink*. 
Steady-State

- For most geochemical reservoirs, there is a constant flow of material both to and from that reservoir.
- If the flow out is greater than the flow in, the mass of the reservoir will decrease and visa versa.
- If the flux in and the flux out are equal, the mass of the reservoir will not change. In this case, it is said to be *steady-state*.

Residence Time

- For a steady-state reservoir, we may define a residence time, which is the average time a molecule or atom (or any other unit) of the substance spends in that reservoir. The residence time can be calculated as:

\[
\tau = \frac{M_e}{dM_e/dt}
\]

- \( \tau \) is the residence time, \( M_e \) is the mass of the element in the reservoir, \( dM_e/dt \) is the flux into or out of the reservoir.
- In English, the residence time is the mass of substance in the reservoir divided by the flux into that reservoir.
The Oceans

- The oceans play a key role in life, geochemical cycling, and climate. They also illustrate these concepts of geochemical cycling and demonstrate the intricate link between life and the physical world.

The Oceans as a Geochemical System

- Why the Sea is Salty
  - Lavoisier: *Oceans are “the rinsings of the Earth”*
  - Ocean salt is a bi-product of weathering on the continents
    \[2\text{NaAlSi}_3\text{O}_8 + 3\text{H}_2\text{O} = \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 4\text{SiO}_2 + 2\text{Na}^+ + 2\text{OH}^-\]
    (Albite Feldspar + Water = Kaolinite + Quartz + alkaline solution)
  - Elements such as Cl, S, etc. are not accounted for by weathering. These volatile elements are the products of volcanic degassing rather than weathering.
Seawater Composition

- Seawater has on average 34.8‰ (parts per thousand) dissolved solids.
- The dissolved solid content of seawater is called its salinity. Salinity varies only because of dilution (by addition of rain or river water) and concentration (resulting from evaporation or freezing).
  - Chlorinity (which is the total of F, Cl, Br, and I) is another measure of the salt content. Average chlorinity is 19.2‰.
- Salinity is important because it, along with temperature, control density, and hence vertical motion of water.

### Principal Salts in the Ocean

<table>
<thead>
<tr>
<th>Anion</th>
<th>% at Cl = 19‰</th>
<th>% dissolved solids</th>
<th>Cation</th>
<th>% at Cl = 19‰</th>
<th>% dissolved solids</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>18.98</td>
<td>55.05</td>
<td>Na</td>
<td>10.57</td>
<td>30.61</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>2.65</td>
<td>7.68</td>
<td>Mg</td>
<td>1.27</td>
<td>3.69</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>0.14</td>
<td>0.41</td>
<td>Ca</td>
<td>0.40</td>
<td>1.16</td>
</tr>
<tr>
<td>Br</td>
<td>0.065</td>
<td>0.19</td>
<td>K</td>
<td>0.38</td>
<td>1.1</td>
</tr>
<tr>
<td>H₃BO₄</td>
<td>0.026</td>
<td>0.07</td>
<td>Sr</td>
<td>0.008</td>
<td>0.03</td>
</tr>
<tr>
<td>F</td>
<td>0.001</td>
<td>0.003</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- These salts (with the exception of bicarbonate) are present in constant proportions.
- Such elements are said to be conservative.
- Constant concentration a result of
  - high abundance
  - unreactivity of these elements
Ocean Thermal Structure

- Characterized by warm mixed surface layer (100-200 meters deep), a thermocline to about 1000 m, and nearly constant temperature below that.
- Thermocline may partly break down in winter in temperate latitudes and is not present in high latitudes.
- Resulting density stratification inhibits vertical exchange.

Two box model of the oceans.

- Exchange between the 2 boxes is limited to upwelling, downwelling, and sinking particles.
- Since light only penetrates ~100 m depth, all photosynthesis occurs in surface layer.
- All atmospheric exchange and atmospheric and riverine inputs occur in surface layer. Only in this zone can changes in Temperature and Salinity occur. Hence, temperature and salinity are said to be conservative.
- The surface water is only 3.5% of total ocean.
Biological Productivity and CO$_2$

- Key Processes: Photosynthesis and Respiration
  - Photosynthesis converts CO$_2$ to organic carbon; respiration does the reverse.
    - Respiration occurs everywhere, but photosynthesis occurs only in surface water.
  - There is a net conversion of CO$_2$ to organic carbon in the surface water.
  - Some fraction of this organic carbon sinks into the deep ocean.
    - Most of this organic carbon is oxidized (respired) before it can be buried in sediment.
- Also Precipitation and Dissolution of CaCO$_3$
  - Many planktonic organisms build shells of CaCO$_3$, which sink when the organism dies.
  - These shells partly redissolve in deep water.

The Biological Pump

- Consequences of the distribution of photosynthesis and respiration in the ocean:
  - Falling organic particles results in the transport of carbon from surface to deep water.
  - This process is called the **biological pump**.
  - The biological pump enhances transport of CO$_2$ from atmosphere and ocean and effectively removes (sequesters) a large amount of CO$_2$ from climate system. Without it, atmospheric CO$_2$ levels would be double what they are.
Nutrients and Their Distribution

- Definition: elements essential to life.
- In addition to H, C, and O, P and N (most "plants" can utilized only "fixed" nitrogen: NO, N₂O, and NH₃) are the most important. Photosynthetic organisms take up dissolved inorganic nutrients to meet their needs.
- Phytoplankton use essentially all available fixed N and P in surface water, resulting in strong surface depletion. These nutrients are released to solution when organic matter is oxidized in deep water.

Micro-Nutrients

- Other elements show similar “nutrient” type profiles.
  - Si used by diatoms (principal photosynthetic organism in oceans) to build shells and is strongly depleted in surface water.
  - Other surface-depleted nutrients include Mn, Fe, Cu, Zn, V, Cr, Ni, Se, and I.
- In addition, biota take up a number of elements incidentally: e.g., Sc, Ge, As, Pd, Ag, Cd, Ba.
- Other elements (B, Na, Mg, S, Cl, K, Ca, Mo, F and Br) are utilized, but no vertical variation results because only a small fraction of the amount available is used.
Nutrient Distribution and Biological Productivity

• The ocean circulation pattern results in horizontal gradients in nutrient abundances. Deep water continually accumulates nutrients, thus “old” deep water, e.g., Pacific, is nutrient-rich, “young” deep water, e.g., Atlantic, is nutrient poor.

• Nutrient availability, together with light, limit biological productivity in surface water.
  – Productivity is high where upwelling returns deep water to surface.
  – In some regions, notably equatorial Pacific, Subarctic and Antarctic, it appears availability of Fe limits productivity.